Journal of Achievements in Materials and Manufacturing Engineering

VOLUME 15
ISSUE 1-2
March-April
2006

Mechanical properties of multilayer coatings deposited by PVD techniques onto the brass substrate

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Received 15.11.2005; accepted in revised form 15.02.2006

Properties

ABSTRACT

Purpose: This research was done to investigate the mechanical properties of coatings deposited by PVD techniques onto brass substrate.

Design/methodology/approach: The coatings were produced by reactive dc magnetron sputtering. The microstructure of the coatings was cross section examined using scanning electron microscope. The residual stress was obtained from the parabolic deflection of the samples, after the coating deposition applying Stoney's equation. The microhardness and Young's modulus tests were made on the dynamic ultra-microhardness tester. Tests of the coatings' adhesion to the substrate material were made using the scratch test.

Findings: Obtained results show that all the coatings are in a state of compressive residual stress. The lower values of the internal stresses in multilayer coatings result from the possibility of stress release in the successive alternating layers of the relatively soft titanium. Highest hardness values are obtained in monolayer coatings. The stiffness of the examined coatings is between 195 ÷ 330 mN/μm, while Young's modulus is between 210 ÷ 348 GPa. Concerning the adhesion of the coatings measured by scratch test, it has been stated that the critical load L_{C2} for coatings, deposited onto the brass ranges from 40 to 50 N. The greatest critical load has been obtained for monolayer coatings.

Research limitations/implications: In order to evaluate with more detail the possibility of applying these coatings in tools, further investigations should be concentrated on the determination of the tribological properties of the coatings.

Practical implications: The tools and functional materials coated by the PVD process have shown significant improvement. Good properties of the PVD coatings make these coatings suitable for various technical and industrial applications.

Originality/value: It should be stressed that the mechanical properties of the PVD coatings obtained in this work are very encouraging and therefore their application for products manufactured at mass scale is possible in all cases where reliable, very hard and abrasion resistant coatings, deposited onto brass substrate are needed.

Keywords: Thin & thick coatings; Residual stresses; Scratch test; Young's modulus; Microhardness

1. Introduction

The development in the scope of producing and increasing the exploitative durability of constructional elements and instruments that are used in different areas, takes place mainly by the use of different techniques of depositing thin layers of hard, wear resistant and corrosion resistant ceramic materials. The required functional properties, the materials and the production techniques should take into account economic considerations. A great selection of available kinds of coatings as well as deposition technologies, is the result of an increasing demand for modern methods of modification and protection of the surface of products. Physical vapour deposition (PVD) techniques are among of those used for this purposes [1-5].

The rapid development of PVD processes allowed the production of coatings with adequate properties for specific applications. The coatings deposited by PVD techniques are used in optics and microelectronics [6-8], biomedicine [9], aeronautics and cosmic industry [10], car industry [11], building industry and housing policy [12,13], as well as mechanical engineering [14].

There is a classification of PVD coatings to be used in mechanically aggressive situations [15,16]:

- coatings of the first generation, which typical example is a titanium nitride TiN with 2000 HV hardness,
- coatings of the second generation that characterize high microhardness (3500-6000HV), resistance to tribological consumption and high temperatures (up to 700C); The typical representatives for this group of coatings are a titanium carbonitride Ti(C,N), a titanium and aluminium nitride (Ti,A1)N as well as diamond like carbon coatings (DLC),
- coatings of the third generation, including multicomponent , multilayer and gradient coatings with required qualities, depending on the use,
- coatings of the fourth generation that change their properties according to required surroundings; the research is carried on the coatings of this generation.

Brass is one of the most widespread technical alloys due to its good usable and technological properties and relatively low price in comparison with other copper alloys. Recently, there has been a tendency not only to improve the properties of brass by using appropriate plastic or heat treatment, but also to increase their usable properties by depositing onto their surface protective coatings by PVD processes [17]. The deposition of protective coatings naturally replaces widely used electrolytic coatings, which present great environmental risk. One of the restrictions for using hard coatings on relatively soft substrates is the arising of high stresses in the coatings themselves and in interface substrate-coating. Thus the estimation of internal stresses that appear in coatings deposited by PVD techniques seems to be an important issue. The mechanical properties like hardness, adhesion and wear resistance of the deposited layers are strongly dependent on the value and of internal stresses. These stresses arise under the influence of the misfit between the coating and the substrate as a result of temperature gradient, of rapid solidification as well as of intensity ion bombardment. Excessive tensile stresses may cause cracking spreading across layers while high compressive stresses may lead to delamination of layers from the surface onto which they had been deposited. It is necessary, then, to define internal stresses in the coatings as an important controlling element of the quality of the deposited coatings.

The aim of this work is the investigation of the mechanical properties of coatings deposited by PVD techniques onto brass substrate.

2. Experiments

The coatings were produced by reactive dc magnetron sputtering using pure metallic targets. They were deposited onto CuZn40Pb2 brass substrates. The nitride coatings, in the case of monolayer coatings, or nitride layers, in the case of the multilayer coatings, were deposited onto the substrates situated in front of the target in Ar and N_2 atmosphere. The metallic layers in the multilayer coatings were deposited an Ar atmosphere. Some deposition conditions are summarized in Table 1.

Targets containing pure metals (Ti, Cr, Mo, Zr) and the Ti - 50% Al alloy were used for the deposition of the coatings.

Metallographic examinations were made on the coated brass specimens and on the brass alone on the LEICA MAEF4A light microscope with the Leica-Qwin computer image analysis system at magnifications up to 1000 ×. The microsections were prepared using STRUERS equipment, and afterwards they were etched in a ferric chloride aqueous solution (10 ml ferric chloride, 30 ml hydrochloric acid, and 100 ml distilled water) to reveal the brass structure.

The structures of the deposited coatings were examined on transverse sections in a Philips XL-30 scanning electron microscope. Secondary electrons were used for generation of fracture images. The accelerating voltage was 20 kV and the maximum magnification was 10000 ×. The notched specimens were cooled in liquid nitrogen before fracturing to eliminate plastic deformation and to ensure brittle fracture.

The thickness of coatings was determined using the “kalotest” method, consisting in measuring the characteristic features of the crater developed in the coated specimen’s surface. The coating thickness was determined by using the following relationship relevant to this setup:

$$g = \frac{D^2 - d^2}{8 \cdot R} \cdot 10^3 \qquad (1)$$

where:
g – coating thickness [μm];
d – crater inner diameter [mm];
D – crater outer diameter [mm];
R – ball diameter [mm].

It is generally assumed that the residual stresses σ_{res} in thin coatings consist of external (σ_{ext}) and internal (σ_{int}) stresses [18]:

$$\sigma_{res} = \sigma_{ext} + \sigma_{int} \qquad (2)$$

The external stresses (thermal stresses) arise as the result of the differences of the values of the thermal expansion coefficients of the coating and the substrate according to:

Table 1
Deposition parameters of the coatings

Coating type	Substrate bias voltage, [V]	Partial pressure, [Pa] N_2	Partial pressure, [Pa] Ar	Number of layers
Ti/CrN × 1 Ti/CrN × 15 Ti/CrN × 150	-50	0*, 0.15**	0.31	1 15 150
Ti/ZrN × 1 Ti/ZrN × 15 Ti/ZrN × 150	-50	0*, 0.10**	0.29	1 15 150
Ti/TiAlN × 1 Ti/TiAlN × 15 Ti/TiAlN × 150	-40	0*, 0.10**	0.38	1 15 150
TiAlN/Mo × 1 TiAlN/Mo × 15 TiAlN/Mo × 150	-60	0*, 0.11**	0.45	1 15 150

*during metallic layers deposition, ** during ceramic layers deposition
During deposition the substrate temperature was always 300°C

$$\sigma_{ext} = \left[E_c/(1-\nu_c)\right]\cdot\Delta\alpha\cdot\Delta T \qquad (3)$$

where:
E and υ – Young's modulus and Poisson ratio for the coating;
Δα - difference between the thermal expansion coefficient of the coating and the substrate;
ΔT - difference between the process temperature and the room temperature.

Techniques used for measurements of the residual stresses are based on the deflection the thin specimens after the coating deposition process. The dimensions of the brass substrates for residual stress measurements were: diameter of 25 mm and thickness of 500 μm. The curvature radius of the coated and uncoated specimens was measured by laser triangulation over the specimen surface in two perpendicular directions (Fig. 1). The residual stresses σ_{res} were calculated using the Stoney's equation [19]:

$$\sigma_{res} = -\frac{E_s \cdot t_s^2}{6\cdot t_c\cdot(1-\upsilon_s)}\left(\frac{1}{r_a}-\frac{1}{r_b}\right) \qquad (4)$$

where:
E_s, t_s and υ_s – Young`s modulus, thickness, and Poisson ratio of the substrate (respectively);
t_c – coating thickness;
r_a and r_b – the specimen surface curvature radii before and after the deposition of the coating.

The microhardness tests were made on the SHIMADZU DUH 202 dynamic ultra-microhardness tester. The tests were made under the load 25 mN, enabling the operator to minimize the influence of the substrate on the obtained results, so that the indentation depth was lower than 1/10 of the thickness of the deposited coatings.

The Young's modulus was calculated using the Hardness 4.2 software package delivered as a part of the ultra-microhardness tester system, according to the formula:

$$\frac{1}{E_r} = \frac{1-\upsilon_i^2}{E_i} + \frac{1-\upsilon_s^2}{E_s} \qquad (5)$$

where:
E_r – reduced Young`s modulus [kN/mm^2];
E_s, E_i – Young`s moduli of the substrate and indenter (respectively) [kN/mm^2];
υ_s, υ_i – Poisson ratio of the substrate and indenter (respectively).

Tests of the coatings' adhesion to the substrate material were made using the scratch test, routinely employed in case of the coatings obtained in processes of physical vapour deposition.

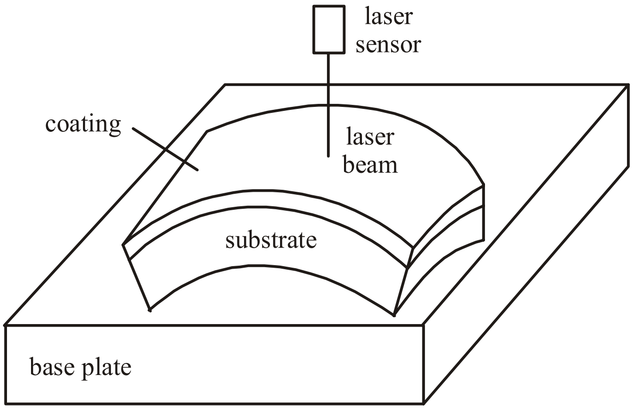

Fig. 1. The schema of the laser triangulation apparatus to measure the curvature radius of the specimens in order to determine the residual stresses.

In this method, the diamond indenter with the Rockwell C type tip with the radius of 200 μm travels on the examined specimen's surface at a constant speed with the continuously increasing load force. The tests were made on the computer controlled Sebastian 5A (Quad Group) device equipped with the acoustic detector, at the following conditions:

- load increase rate (dL/dt) – 100 N/min;
- indenter feed rate (dx/dt) – 10 mm/min.

3. Discussion of results

It was confirmed in metallographic examinations made on the light microscope that the investigated coatings were deposited onto the diphase (α+β) CuZn40Pb2 brass substrate using the reactive magnetron sputtering PVD technique. These coatings are characterised by uniform thickness on their entire area and good adhesion to the substrate (Fig. 2). The diphase CuZn40Pb2 brass structure, visible in the pictures consists of the α phase (light grains), β phase (dark grains) and of the fine grained, uniformly distributed Pb precipitations.

Fractographic examinations of the investigated coatings' fractures, made in the electron scanning microscope, confirmed the initial statement that the coatings were correctly deposited. The coatings display compact structure without visible delamination or defects. In case of the single layer coatings their columnar structure is clearly visible (Fig. 3).

Examination of the multilayer coatings' fractures in the scanning electron microscope indicates the lack of the columnar structure. It was confirmed by SEM the alternating ceramic/metallic layers (Fig. 4).

The critical load L_{C2} characterizes the adhesion of examined coatings to the CuZn40Pb2 brass substrate. A summary result is presented in table 2. The critical load L_{C2} has been established as corresponding to the rapid fall of the acoustic emission due to friction force change between a diamond indenter and the partially crumbled coating (Fig. 5). It has also been established on the basis of optical observations made on the light microscope.

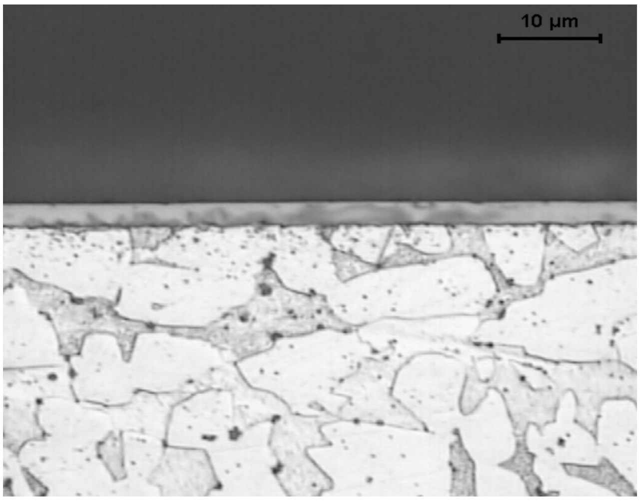

Fig. 2. TiAlN/Mo × 15 coating deposited onto the CuZn40Pb2 substrate

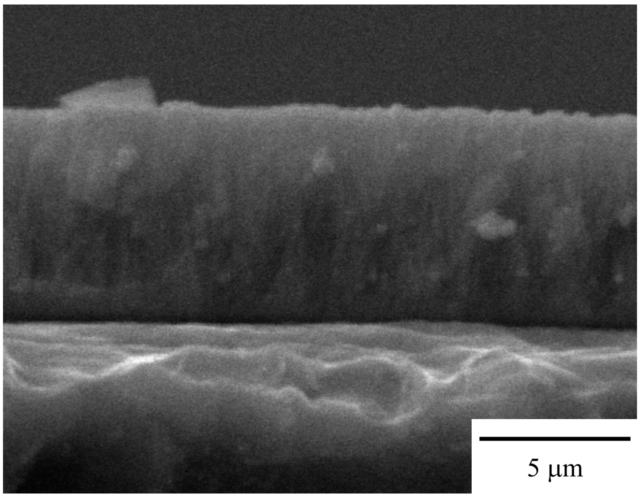

Fig. 3. SEM micrograph of fracture in TiAlN/Mo × 1 sample.

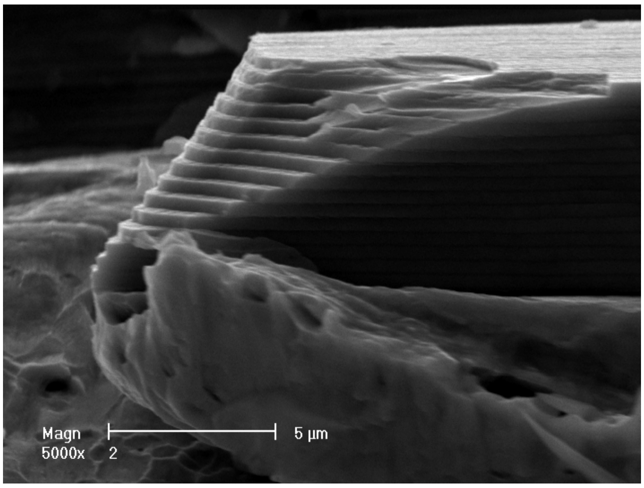

Fig. 4. SEM micrograph of fracture of the Ti/CrN × 15 sample.

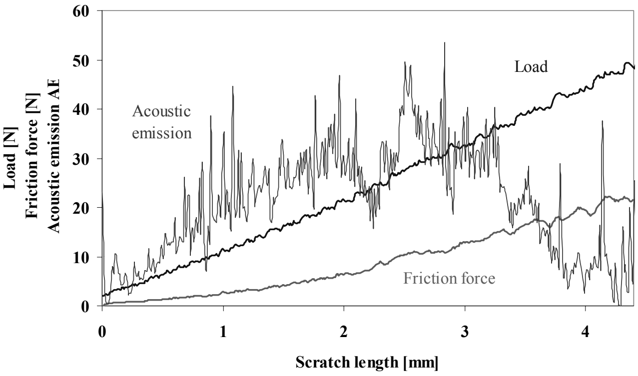

Fig. 5. Plot of the dependence of the acoustic emission and friction force from the scratch path for the Ti/TiAlN×1 coating deposited onto the CuZn40Pb2 substrate.

Based on these results, one can say that the critical load L_{C2}, at which the coating failure occurs becomes smaller along with the increase of the number of layers in the coating. Employment of the additional, thin metallic interlayer (Ti, Mo) for monolayer coatings, gives better adhesion of the nitride coating to the substrate as it counteracts propagation of cracks and reduces stresses in the coating-substrate zone [20]. In case of multilayer coatings, as a result of the pressure of the indenter onto the coating, there is the deformation of the coating, as softer and more elastic layers undergo greater deformation than hard nitride coatings. This is how bending stresses are generated which cause the destruction of the system of alternating hard and soft layers due to the nitride coating layers subjected to excessive strain. The relatively softer and more elastic layers from pure metals are not able to counteract wear effectively when in contact with other materials like in case of hard layers.

The use of hard layers on soft substrates causes the formation of high stresses in the coatings as well as along the substrate-coating interface when the coating is loaded or the substrate is bending [21].

The obtained results show that the coatings are under compressive (negative) residual stress (Table 2). In this case the dominant role is played by the internal stresses, connected to the growing process itself. The external (thermal) stresses are not significant because the deposition temperatures are relatively low. The residual stress in multilayer coatings is lower than in monolayer coatings (table 2). This is due to the stress release occurring in the ductile metallic layers. The compressive stresses in the coatings, within certain limits, cause the increase of their endurance properties and especially hardness. Too big compressive stresses may, however, cause adhesion problems, as in case of Ti/TiAlN×1 and Ti/ZrN×1 coating (Table 2), especially close to the edge, which results in delamination or chipping phenomena (Fig. 6).

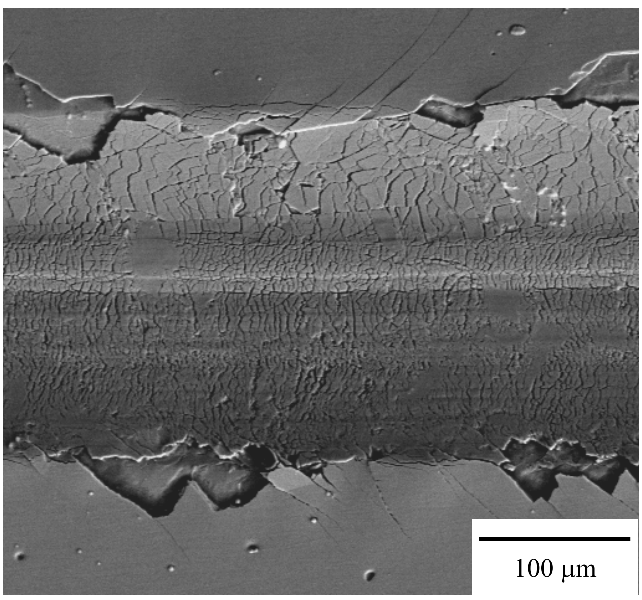

Fig. 6. Characteristic failure of the Ti/TiAlN×1 coating developed during the adhesion „scratch test”, SEM.

Hardness tests of the deposited coatings were made in the ‘load-unload’ mode, in which loading of the indenter with a specified force takes place, holding it for the predetermined time, and then the indenter load force is released (Fig. 7). When carrying out the test, one can observe not only plastic deformation of the material but also its elastic deformation. Microhardness determined this way is called dynamical microhardness. The precise meter circuit allows registering the depth of the created imprint while loading or unloading the indenter.

With the use of the Hardness 4.2 software package, which is part of the ultramicrohardness tester, and the dependency between the load and the depth of the indenter into the examined coating (Fig. 7,8), the Young’s modulus as well as the stiffness of coatings, have been determined (Table 2). The stiffness of the examined coatings is between 195 ÷ 330 mN/µm, whereas Young’s modulus is between 210 ÷ 348 GPa. As in the case of hardness results, the Young’s modulus decreases with the increase of the number of layers.

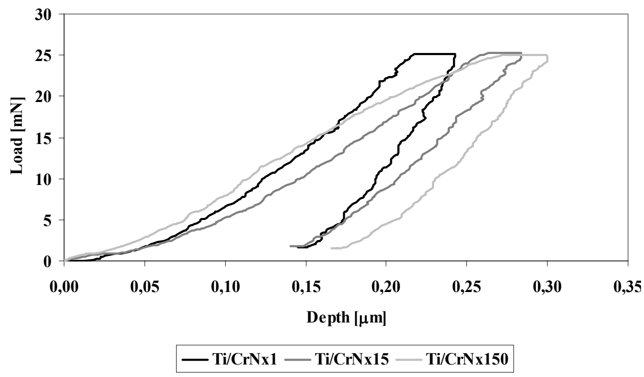

Fig. 7. Plot of the load/unload curves as a function of the depth for Ti/CrN coatings.

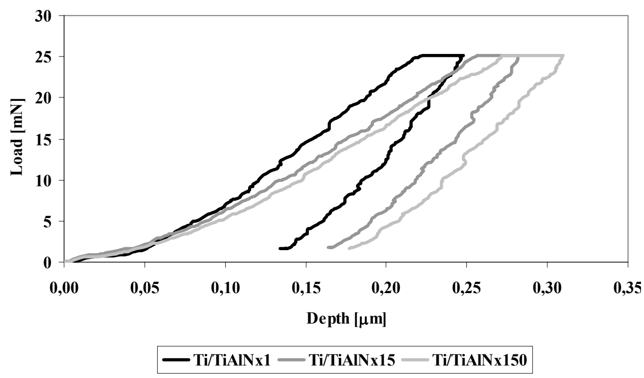

Fig. 8. Plot of the load/unload curves as a function of the depth for Ti/TiAlN coatings.

A clear decrease of hardness with the increase of the number of layers was revealed (Table 2). The highest hardness was obtained for monolayer coatings. With the increase of the number of layers, coating hardness decreases. It is due to higher hardness

Table 2
Summary results of the mechanical properties

Coating type	Residual stresses, GPa	Critical load L_{C2}, N	Hardness DHV0,0025	Young`s modulus, GPa	Stiffness, mN/μm	Thickness, μm
Ti/CrN × 1	-2.6	50	2450	258	330	5.8
Ti/CrN × 15	-2.3	48	2350	235	251	4.5
Ti/CrN × 150	-0.1	47	1800	228	216	3.1
Ti/ZrN × 1	-8.9	45	3100	291	224	2.1
Ti/ZrN × 15	-4.7	41	2700	343	265	1.6
Ti/ZrN × 150	-1.6	40	2200	290	253	1.9
Ti/TiAlN × 1	-11.9	41	2400	348	274	2.3
Ti/TiAlN × 15	-2.1	40	2100	259	253	2.7
Ti/TiAlN × 150	-0.2	38	1850	210	195	2.2
TiAlN/Mo × 1	-1.3	48	2400	302	236	6.2
TiAlN/Mo × 15	-1.3	45	2200	293	226	6.5
TiAlN/Mo × 150	-0.1	40	2000	297	250	5.9

of a single nitride layer, e.g. ZrN or TiN, than of a X/XN system of 15 to 150 layers, where properties and hardness of the alternating (soft) X metallic layer and the XN nitride layer (hard) are different.

4. Summary

All the coatings are under compressive residual stress. These results are related with measured elastic modulus, hardness and adhesion. The lower values of internal stresses in multilayer coatings result from the possibility of stress release in successive alternating layers of relatively soft titanium.

Hardness, as expected, reaches the greatest values for monolayer coatings. The main reason for this is greater hardness of a single nitride layer than that of the system of 15 or 150 alternating hard and soft layers, which cause the fall of the average multilayer coatings hardness and greater values of internal stresses for monolayer coatings.

The stiffness of the examined coatings is between 195 ÷ 330 mN/μm, while Young's modulus is between 210 ÷ 348 GPa.

Concerning the adhesion of the coatings measured by scratch test, it has been stated that the critical load L_{C2} for coatings deposited onto the brass ranges from 40 to 50 N. The greatest critical load has been obtained for monolayer coatings.

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